

Flame-hydrolytically Produced Titanium Dioxide Powder

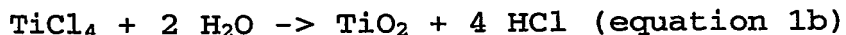
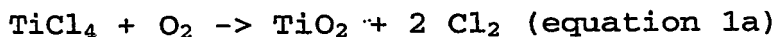
The invention relates to flame-hydrolytically produced titanium dioxide powder, and its production and use.

5

It is known that titanium dioxide can be produced by pyrogenic processes. Pyrogenic processes are understood to include flame oxidations or flame hydrolyses. In flame oxidation a titanium dioxide precursor, for example titanium tetrachloride, is oxidised with oxygen according to equation 1a. In flame hydrolysis the formation of titanium dioxide is effected by hydrolysis of the titanium dioxide precursor, the water necessary for the hydrolysis being derived from the combustion of a fuel gas, for example hydrogen, and oxygen (equation 1b).

10

15



20

EP-A-1231186 claims a titanium dioxide with a BET surface of between 3 and 200 m²/g with a weight-related D₉₀ diameter of the particles of 2.2 µm or less. D₉₀ diameters of between 0.8 and 2.1 µm are mentioned in the examples of implementation. In addition, a titanium dioxide is obtained with a BET surface of between 3 and 200 m²/g and a distribution constant n of 1.7 or more, calculated according to the formula $R = 100 \exp(-bD^n)$, where D denotes the particle diameter and b is a constant. The value n is obtained from the three values D₁₀, D₅₀ and D₉₀, which are related to one another by an approximate straight line. The titanium dioxide is obtained by a flame oxidation of titanium tetrachloride and an oxidising gas, the starting

25

30

materials being pre-heated to a temperature of at least 500°C before the reaction. In preferred embodiments the velocity of the reaction mixture is 10 m/sec or more, and the residence time in the reaction space is 3 sec or less.

5

In EP-A-778812 a process for the production of titanium dioxide by a combination of flame oxidation and flame hydrolysis is described. In this connection titanium tetrachloride in the vapour state and oxygen are mixed in a reaction zone and the mixture is heated in a flame that is generated by combustion of a hydrocarbon as fuel gas. The titanium tetrachloride is fed into the central core of the reactor, the oxygen is fed into a tubular sleeve surrounding the central core, and the fuel gas is fed into a tubular sleeve that surrounds those tubes that convey the titanium tetrachloride and oxygen.

A laminar diffusion flame reactor is preferably employed. In this method it is possible to produce highly surface-active titanium dioxide powder containing a large proportion of the anatase modification. In EP-A-778812 no information is given regarding the structure and size of the primary particles and aggregates. However, it is these quantities in particular that are important for many applications, for example in cosmetics applications or as an abrasive in dispersions for the electronics industry. The mechanism of the formation of the titanium dioxide according to EP-A-778812 includes both a flame oxidation (equation 1a) as well as a flame hydrolysis (equation 1b). Although the different formation mechanisms enable the anatase fraction to be controlled, a specific distribution of the primary particles and aggregates cannot however be achieved. A further disadvantage of this method, as is

mentioned in US-A-20002/0004029, is the incomplete conversion of titanium tetrachloride and fuel gas and the resultant grey colouration of the titanium dioxide.

- 5 These problems are eliminated according to US-A-20002/0004029, by now using five tubes instead of the three tubes as described in EP-A-778812. For this, titanium tetrachloride vapour, argon, oxygen, hydrogen and air are simultaneously metered into a flame reactor. The
- 10 disadvantage of this method is the use of the expensive noble gas argon and a low yield of titanium dioxide due to low concentrations of titanium tetrachloride in the reaction gas.
- 15 A titanium dioxide powder produced by flame hydrolysis has for a long time been marketed by Degussa under the reference P 25.

This is a finely particulate titanium dioxide powder with a

20 specific surface of $50 \pm 15 \text{ m}^2/\text{g}$, a mean size of the primary particles of 21 nm, a compacted bulk density (approximate value) of 130 g/l, an HCl content of less than or equal to 0.300 wt.% and a screening residue according to Mocker (45 μm) of less than or equal to 0.050%. This powder has

25 good properties for many applications.

The prior art demonstrates the wide interest in pyrogenically produced titanium dioxide. In this connection it is found that the common generic term

30 "pyrogenic", i.e. flame hydrolysis and flame oxidation, is not an adequate description of titanium dioxide. On account of the complexity of the pyrogenic processes only a few substance parameters can be specifically adjusted.

Titanium dioxide is employed in particular in catalysis, for example photocatalysis, in cosmetics, for example sunscreen agents, as an abrasive in the form of dispersions in the electronics industry, or for heat stabilisation of polymers. In these uses increasing demands are placed on the purity and structure of the titanium dioxide. Thus, it is for example important that, when using titanium dioxide as an abrasive in dispersions, the titanium dioxide has a good dispersibility and is as far as possible free from coarse particles that can scratch the surface to be polished.

The object of the present invention is to provide a titanium dioxide powder that has a high purity, is easy to disperse, and is as far as possible free of coarse fractions.

The object of the present invention is also to provide a process for the production of the titanium dioxide powder. In this connection the process should be able to be implemented on an industrial scale.

The present invention provides a flame-hydrolytically produced titanium dioxide powder that is present in aggregates of primary particles, characterised in that

- it has a BET surface of 20 to 200 m²/g and
- the half width HW, in nanometers, of the primary particle distribution has values between

$HW [nm] = a \times BET^f$ where $a = 670 \times 10^{-9} \text{ m}^3/\text{g}$ and
 $-1.3 \leq f \leq -1.0$ and

- 5 - the proportion of particles with a diameter of more than 45 μm is in a range from 0.0001 to 0.05 wt.%.
1

The term primary particles in the context of the invention is understood to denote particles that are first of all formed in the reaction and that can coalesce to form aggregates during the further course of the reaction.
10

The term aggregate within the context of the invention is understood to denote primary particles of similar structure and size that have coalesced together, and whose surface is smaller than the sum of the individual, isolated primary particles. Several aggregates or also individual primary particles may combine together further to form agglomerates. Aggregates or primary particles accordingly lie adjacent to one another in the form of point objects.
15
20 Depending on their degree of coalescence, agglomerates may be broken up by application of energy.

Aggregates on the other hand can be broken up only by a high input of energy or even cannot be broken up at all.
25 Intermediate forms exist.

The mean half width HW of the primary particle distribution (in numerical terms) is obtained by image analysis of the TEM photographs. According to the invention the mean half width is a function of the BET surface with a constant f, where $-1.3 \leq f \leq -1.0$. Preferably the half width may lie in the range $-1.2 \leq f \leq -1.1$.
30

It is the high BET surface, the narrow distribution of the primary particle distribution and the low proportion of aggregates with a diameter of more than 45 μm , which lies in a range from 0.0001 to 0.05 wt.%, that are relevant for the positive properties of the powder according to the invention, for example when polishing surfaces. No flame-hydrolytically produced titanium dioxide powders are known in the prior art that simultaneously exhibit these features. It is of course possible for example to remove to a large extent powders according to the prior art mechanically from aggregates with a diameter of more than 45 μm , though the resultant powder would however not be able to achieve the ranges claimed by the present invention as regards BET surface and half width values of the primary particles.

The BET surface of the titanium dioxide powder according to the invention lies in a wide range from 20 to 200 m^2/g . It has proved advantageous if the BET surface lies in a range from 40 to 60 m^2/g . A range of 45 to 55 m^2/g may be particularly advantageous.

For a titanium dioxide powder according to the invention with a BET surface between 40 and 60 m^2/g , the 90% spread of the number distribution of the primary particle diameters may lie between 10 and 100 nm. As a rule the 90% spread of the number distribution of the primary particle diameters is between 10 and 40 nm.

Furthermore, the equivalent circular diameter of the aggregates (ECD) of such a titanium dioxide powder may be less than 80 nm.

The mean aggregate area of a titanium dioxide powder according to the invention with a BET surface of 40 to 60 m²/g may be less than 6500 nm² and the mean aggregate circumference may be less than 450 nm.

5

In addition the BET surface of the titanium dioxide powder according to the invention may lie in a range from 80 to 120 m²/g. A range of 85 to 95 m²/g may be particularly preferred.

10

For a titanium dioxide powder according to the invention with a BET surface between 80 and 120 m²/g, a 90% spread of the number distribution of the primary particle diameters may have values between 4 and 25 nm. Furthermore, such a titanium dioxide powder may have an equivalent circular diameter of the aggregates (ECD) of less than 70 nm.

15

The mean aggregate area of a titanium dioxide powder according to the invention with a BET surface of 80 to 120 m²/g may be less than 6000 nm² and the mean aggregate circumference may be less than 400 nm.

20

The proportion of aggregates and/or agglomerates of the titanium dioxide powder according to the invention with a diameter of more than 45 µm lies in a range from 0.0001 to 0.05 wt.%. A range from 0.001 to 0.01 wt.% may be preferred, and a range from 0.002 to 0.005 wt.% may be particularly preferred.

25

The titanium dioxide powder according to the invention comprises rutile and anatase as crystal modifications. In this connection the anatase/rutile proportion for a given surface may lie in a range from 2:98 to 98:2. The range from 80:20 to 95:5 may be particularly preferred.

30

The titanium dioxide powder according to the invention may contain residues of chloride. The chloride content is

35

preferably less than 0.1 wt.%. A titanium dioxide powder according to the invention with a chloride content in the range from 0.01 to 0.05 wt.% may be particularly preferred.

- 5 The compacted bulk density of the titanium dioxide powder according to the invention is not limited. It has however proved advantageous if the compacted bulk density has values from 20 to 200 g/l. A compacted bulk density of 30 to 120 g/l may be particularly preferred.

10

The present invention also provides a process for the production of the titanium dioxide powder according to the invention, which is characterised in that

- 15 - a titanium halide, preferably titanium tetrachloride, is vapourised at temperatures of less than 200°C, the vapours are transferred to a mixing chamber by means of a carrier gas with a proportion of steam in a range from 1 to 25 g/m³, and
- 20 - separately from this, hydrogen, primary air, which may optionally be enriched with oxygen and/or pre-heated, and steam are transferred to the mixing chamber,
- 25 - wherein the proportion of steam is in a range from 1 to 25 g/m³ primary air,
- the lambda value lies in the range from 1 to 9 and the gamma value lies in the range from 1
- 30 to 9,

following which

- 35 - the mixture consisting of the titanium halide vapour, hydrogen, air and steam is ignited in a burner and the flame burns back into a reaction chamber sealed from

the ambient air, wherein

- a vacuum of 1 to 200 mbar exists in the reaction chamber,

5

- the exit velocity of the reaction mixture from the mixing chamber to the reaction space lies in a range from 10 to 80 m/sec,

- 10 - in addition secondary air is introduced into the reaction chamber, wherein

- the ratio of primary air to secondary air is between 10 and 0.5,

15

- following which the solid is separated from gaseous substances, and

- the solid is then treated with steam.

20

An essential feature of the process according to the invention is that the titanium halide is vapourised at temperatures below 200°C and the vapours are conveyed to the mixing chamber by means of a carrier gas, for example
25 air or oxygen, which has a defined carrier gas moisture content. It has been found for example that the product quality decreases at higher vapourisation temperatures.

Moreover it has also been found that, within the claimed
30 steam content of 1 to 25 g/m³ of gas, or primary air, there is no noticeable hydrolysis of the titanium halide in the form of caking, whereas on the other hand the steam content influences the subsequent primary particle and aggregate structure. Outside the claimed range, no powder according
35 to the invention can be obtained. In a preferred embodiment the steam content is between 5 and 20 g/m³ of gas, or primary air.

As carrier gas, air may also be used. This permits a higher space-time yield in the reaction chamber than when using an inert gas.

5

Furthermore, the exit velocity of the reaction mixture from the mixing chamber into the reaction space lies in a range from 10 to 80 m/sec. In a preferred embodiment the exit velocity is between 15 and 60 m/sec, and in a particularly preferred embodiment is between 20 and 40 m/sec. At values below this a uniform powder is not obtained, but instead a powder is obtained that contains particles of diameter 45 μm or more in an amount of more than 0.05 wt.%.
10

15 In addition the reaction must be carried out so that the lambda value lies in the range from 1 to 9 and the gamma value lies in the range from 1 to 9.

Flame-hydrolytically produced oxides are normally obtained so that the gaseous starting substances are in a stoichiometric ratio with respect to one another such that the added hydrogen is at least sufficient to react with the halogen X present from the titanium halide TiX_4 to form HX. The amount of hydrogen required for this purpose is termed the stoichiometric amount of hydrogen.
20
25

The ratio of the added hydrogen to the stoichiometrically necessary hydrogen defined above is termed gamma. Gamma is defined as:

30

Gamma = $\frac{\text{added hydrogen}}{\text{stoichiometrically required hydrogen}}$

or

35

Gamma = $\frac{\text{H}_2 \text{ fed in (moles)}}{\text{H}_2 \text{ stoichiometric (moles)}}$.

With flame-hydrolytically produced oxides in addition an amount of oxygen (for example from the air) is normally used that is at least sufficient to convert the titanium halide into titanium dioxide and to convert excess hydrogen
5 that may still be present into water. This amount of oxygen is termed the stoichiometric amount of oxygen.

Similarly, the ratio of added oxygen to stoichiometrically required oxygen is termed lambda, and is defined as
10 follows:

$$\text{Lambda} = \text{added oxygen} / \text{stoichiometrically required oxygen}$$

or

15

$$\text{Lambda} = \text{O}_2 \text{ fed in (moles)} / \text{O}_2 \text{ stoichiometric (moles)}.$$

Moreover, in the process according to the invention, in addition to the primary air in the mixing chamber air
20 (secondary air) is directly introduced into the reaction chamber. It has been found that, without the addition of the additional air into the mixing chamber, no titanium dioxide powder according to the invention is obtained. In this connection it should be noted that the ratio of
25 primary air to secondary air is between 10 and 0.5. The ratio is preferably in a range between 5 and 1.

In order to be able accurately to meter in the amount of secondary air, it is necessary to cause the flame to burn
30 back into a reaction chamber sealed from the ambient air. This enables the process to be accurately controlled, which is essential in order to obtain the titanium dioxide powder according to the invention. The vacuum in the reaction chamber is preferably between 10 and 80 mbar.

35

An essential feature is also the fact that titanium dioxide powder after separation from gaseous substances should be

treated with steam. This treatment is primarily intended to remove halide-containing groups from the surface. At the same time this treatment reduces the number of agglomerates. The process may be carried out continuously in such a way that the powder is treated, in counter-current or co-current, with steam, possibly together with air, in which connection the steam is always introduced from below into an upright, heatable column. The feed of the powder may take place from the top or the bottom of the column. The reaction conditions may be chosen so that a fluidised bed is formed. The temperature at which the treatment with steam is carried out is preferably between 250 and 750°C, values from 450 to 550°C being preferred. In addition it is preferred to carry out the treatment in counter-current in such a way that a fluidised bed is not formed.

Moreover it may be advantageous to introduce the steam together with the air into the mixing chamber.

Fig. 1A shows diagrammatically an arrangement for carrying out the process according to the invention. In the figure: A = mixing chamber, B = flame, C = reaction chamber, D = solid/gaseous separation, E = post-treatment with steam.

The substances used are identified as follows: a = mixture of titanium halide and carrier gas with defined moisture content, b = hydrogen, c = air, d = steam, e = secondary air, f = steam or steam/air. Fig. 1B shows a section of the arrangement of Fig. 1A. In this, the steam (d) together with the air (c) are introduced into the mixing chamber. Fig. 1C shows an open reaction chamber in which the secondary air e is aspirated from the surroundings. With the arrangement according to Fig. 1C no titanium dioxide powder according to the invention can be obtained.

The invention also provides for the use of the titanium dioxide powder according to the invention for the heat protection stabilisation of silicones.

- 5 The invention in addition provides for the use of the titanium dioxide powder according to the invention in sunscreen agents.

- 10 The invention furthermore provides for the use of the titanium dioxide powder according to the invention as a catalyst, as a catalyst carrier, as a photocatalyst, and as an abrasive for the production of dispersions.

Examples**Analysis**

- 5 The BET surface is determined according to DIN 66131.

The compacted bulk density is determined on the basis of DIN ISO 787/XI K 5101/18 (not screened).

- 10 The bulk density is determined according to DIN-ISO 787/XI.

The pH value is determined on the basis of DIN ISO 787/IX, ASTM D 1280, JIS K 5101/24.

- 15 The proportion of particles larger than 45 μm is determined according to DIN ISO 787/XVIII, JIS K 5101/20.

- Determination of the chloride content: ca. 0.3 g of the particles according to the invention is accurately weighed
20 out, 20 ml of 20 per cent sodium hydroxide solution (analysis purity) are added thereto, dissolved, and transferred while stirring to 15 ml of cooled HNO_3 . The chloride content in the solution is titrated with AgNO_3 solution (0.1 mole/l or 0.01 mole/l).

- 25 The half width of the primary particle distribution and area, circumference and diameter of the aggregates are determined by means of image analysis. The image analyses are carried out using an H 7500 TEM instrument from Hitachi
30 and a MegaView II CCD camera from SIS. The image magnification for the evaluation is 30000 : 1 at a pixel density of 3.2 nm. The number of evaluated particles is greater than 1000. The preparation is carried out according to ASTM3849-89. The lower threshold boundary as
35 regards detection is 50 pixels.

Example A1 (according to the invention)

160 kg/hr of TiCl_4 are vapourised in an evaporator at 140°C .
5 The vapours are transferred to a mixing chamber by means of
nitrogen ($15 \text{ Nm}^3/\text{hr}$) as carrier gas with a carrier gas
moisture content of 15 g/m^3 of carrier gas. Separately from
this, $52 \text{ Nm}^3/\text{hr}$ of hydrogen and $525 \text{ Nm}^3/\text{hr}$ of primary air
are introduced into the mixing chamber. In a central tube
10 the reaction mixture is fed to a burner and ignited. The
flame burns in a water-cooled flame tube. In addition
 $200 \text{ Nm}^3/\text{hr}$ of secondary air are added to the reaction space.
The powder formed is separated in a downstream filter and
then treated in countercurrent with air and steam at 520°C .

15 The **Examples A2 to A9 according to the invention** are
carried out similarly to A1. The parameters altered in
each case are listed in Table 1.

20 The physicochemical data of the powders from Examples A1 to
A9 are shown in Table 2.

The **comparison examples B1 to B3 and B5 to B8** are also
carried out similarly to A1. The parameters altered in
25 each case are listed in Table 1.

The **comparison example B4** is carried out using an open
burner. The amount of secondary air is not determined.

30 The physicochemical data of the powders from Examples B1 to
B8 are shown in Table 2.

Table 3 shows the calculated half width of the primary
particles depending on the BET surface area with $f=-1.0$, -
35 1.05, -1.15 und -1.3. The factor 10^{-9} is the basis for the
conversion of meter into nanometer. As factor f can only be
negative, the unit of BET^f is g/m^2 .

Fig. 2 shows the half width of the primary particles of the titanium dioxide powders produced in the examples. In this connection the titanium dioxide powders according to the invention (identified as ■) lie within the claimed half width $HW [nm] = a \times BET^f$ where $a = 670 \times 10^{-9} m^3/g$ and $-1.3 \leq f \leq -1.0$, while the comparison examples (identified by +) lie outside.

Table 1: Process parameters in the production of the titanium dioxide powders

Ex.	TiCl ₄	T _v	Carrier Gas	Carrier Gas Moisture	H ₂	Primary Air	Primary Air Moisture	Secondary Air	Gamma	Lambda	v	T _z
	kg/h		Nm ³ /h	g/m ³	Nm ³ /h	Nm ³ /h	g/m ³	Nm ³ /h			m/s	°C
A1	160	140	15	15	52	525	15	200	1.38	3.55	27	520
A2	160	140	15	15	52	525	10	200	1.38	3.55	27	650
A3	160	140	3	10	52	635	15	200	1.38	5.15	31	450
A4	160	140	15	10	82	415	15	200	2.17	2.25	23	520
A5	200	140	40	8	52	500	10	200	1.1	4.3	26	520
A6	40	140	15	15	67	535	10	200	7.08	3.44	27	520
A7	40	140	15	6	67	550	10	200	7.08	3.54	27	520
A8	40	140	15	22	60	780	10	200	6.34	5.55	38	520
A9	160	140	15	2	52	225	10	200	1.38	1.93	14	520
B1	160	250	15	10	52	525	10	200	1.38	3.55	27	520
B2	160	140	15	40	52	525	10	200	1.38	3.55	27	520
B3	160	140	15	10	52	1200	12	200	1.37	9.67	56	520
B4	160	140	15	10	52	525	12	**	1.38	3.55	27	520
B5	40	140	15	10	70	560	12	10	7.4	3.35	26	650
B6	160	140	15	10	52	525	12	200	1.38	3.55	27	-
B7	160	140	15	10	52	525	15	0	1.38	3.55	27	520
B8	160	220	15	10	52	525	15	50	1.38	3.55	27	520

T_v = temperature of evaporator; T_z = deacidification temperature; B4: = open burner, no secondary air measurement; v = exit velocity of the reaction mixture from the mixing chamber into the reaction space

Table 2: Physicochemical parameters of the titanium dioxide powders

Ex.	BET	Primary Particles		Aggregates					Anatase	Bulk Density	Compacted Bulk Density	Chlorine Content	pH-Value
		Half Width	ECD	Avg. Area	Avg. Circmf.	Particles > 45 µm							
	m ² /g	nm	nm	nm ²	nm	%	%	g/l	%	g/l	g/l	Wt.%	
A1	48	11.0	67.4	4976	366.3	0.001	89	84	89	84	114	0.02	3.8
A2	47	10.4	66.4	5112	369.5	0.001	89	88	89	88	115	0.15	4.2
A3	49	9.3	65.3	4827	371.9	0.002	85	87	85	87	108	0.1	3.8
A4	24	19.8	n.d.	n.d.	n.d.	0.003	52	96	52	96	114	0.05	4.0
A5	43	13.5	66.5	5140	380.75	0.002	92	88	92	88	110	0.11	3.8
A6	85	5.4	63.1	5017	341.0	0.010	93	102	93	102	122	0.15	3.9
A7	91	4.8	62.4	5314	331.5	0.008	90	99	90	99	125	0.13	3.8
A8	172	2.2	60.1	5128	321.0	0.009	96	115	96	115	158	0.09	3.7
A9	49	34.3	n.d.	n.d.	n.d.	0.002	71	112	71	112	143	0.04	4.0
B1	48	17.2	75.8	6525	448.3	0.019	89	83	89	83	106	0.03	3.8
B2	49	16.0	81.2	6713	481.0	0.025	91	84	91	84	108	0.11	3.9
B3	188	5.9	77.9	6418	452.3	0.004	97	111	97	111	162	0.09	4.0
B4	48	16.6	82.3	7214	474.8	0.010	87	89	87	89	111	0.04	3.9
B5	94	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
B6	51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.51	2.3
B7	49	18.4	n.d.	n.d.	n.d.	0.06	85	n.d.	85	n.d.	n.d.	0.08	3.9
B8	49	19.8	n.d.	n.d.	n.d.	0.11	87	n.d.	87	n.d.	116	0.1	4.0

n.d. = not determined

Tab. 3: Calculated half width of primary particles

BET [m ² /g]	Half width of primary particles [nm]			
	$670 \cdot 10^{-9} \cdot$ BET ^{-1,00}	$670 \cdot 10^{-9} \cdot$ BET ^{-1,05}	$670 \cdot 10^{-9} \cdot$ BET ^{-1,15}	$670 \cdot 10^{-9} \cdot$ BET ^{-1,3}
20	33,50	28,84	21,37	13,64
30	22,33	18,84	13,41	8,05
40	16,75	13,93	9,63	5,54
50	13,40	11,02	7,45	4,14
60	11,17	9,10	6,04	3,27
70	9,57	7,74	5,06	2,68
80	8,38	6,73	4,34	2,25
90	7,44	5,94	3,79	1,93
100	6,70	5,32	3,36	1,68
120	5,58	4,39	2,72	1,33
150	4,47	3,48	2,11	0,99
170	3,94	3,05	1,82	0,84
200	3,35	2,57	1,51	0,68

Heat stabilisation of polymers**Example C1: without titanium dioxide powder (comparison example)**

A two-component silicone rubber from Bayer, trade name Silopren® LSR 2040, is used as base component (addition crosslinking). After homogeneously mixing the two components with a dissolver the vulcanisation takes place at 180 °C for 10 minutes. Sample plates (ca. 10 x 15 cm) 6 mm thick are produced. The sample plates are heated at 80 °C in a furnace to constant weight (ca. 1 day). To check the thermal stability to heat a hot storage test is carried out. For this, a sample strip of size 5 x 7 cm is kept in a circulating air oven at 275 °C. The weight loss is measured.

Example C2: Addition of titanium dioxide powder according to the prior art (comparison example)

A two-component silicone rubber from Bayer, trade name Silopren® LSR 2040, is used as base component (addition crosslinking). 1.5 wt.%, referred to the total batch, of titanium dioxide powder P 25 S (Degussa AG) is incorporated for 5 minutes into one of the components, using a dissolver. Following this the vulcanisation and production of the sample plates take place as described in Example 1.

Sample strips of size 5 x 7 cm are stored at 275 °C. The weight loss is measured.

- 10 The Examples C3-5 are carried out similarly to C1, but using the titanium dioxide powders A1 according to the invention in C3, A3 in C4 and A7 in C5, instead of P25 S.

Table 4 shows the changes in length of the samples stored at 275°C after 1, 3 and 7 days.

- 15 The results demonstrate the effective heat protection stabilisation of polymers achieved by using the titanium dioxide powder according to the invention.

Table 4: Two-component silicone rubber

Example	Length Change [%] after		
	1 Day	3 Days	7 Days
C1 (comp.)	98.6	-	-
C2 (comp.)	46.3	58.9	70.0
C3	16.3	27.9	39.5
C4	18.7	41.8	52.7
C5	29.0	49.0	58.0

Photocatalytic activity

Example D1: Titanium dioxide powder according to the prior art (comparison example)

To determine the photocatalytic activity the sample to be measured is suspended in 2-propanol and irradiated for one hour with UV light. The concentration of acetone formed is then measured.

5 Ca. 250 mg (accuracy 0.1 mg) of titanium dioxide powder P 25S (Degussa AG) are suspended using an Ultra-Turrax stirrer in 350 ml (275.1 g) of 2-propanol. This suspension is conveyed by means of a pump through a cooler
10 thermostatically controlled to 24°C to a glass photoreactor equipped with a radiation source and flushed beforehand with oxygen. An Hg medium-pressure immersion lamp of the type TQ718 (Heraeus) with an output of 500 Watts serves for example as radiation source. A protective tube of
15 borosilicate glass restricts the emitted radiation to wavelengths >300nm. The radiation source is surrounded externally by a cooling tube through which water flows. Oxygen is metered into the reactor via a flow meter. The reaction is started when the radiation source is switched on. At the end of the reaction a small amount of the
20 suspension is immediately removed, filtered, and analysed by gas chromatography.

A photoactivity k of $0.68 \times 10^{-3} \text{ mole kg}^{-1}\text{min}^{-1}$ is measured. This is taken as base value 1. The titanium dioxide powder according to the invention has a somewhat lower
25 photocatalytic activity of 0.8 to 0.9.